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BARIUM AND STRONTIUM TITANATES SYNTHESIZED IN A CONCENTRATED LIGHT FIELD

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It is shown that barium titanate $BaTiO_3$ and strontium titanate $SrTiO_3$ are synthesized when the mixtures $TiO_2 + BaCO_3$ and $TiO_2 + SrCO_3$ are fused in the focal plane of radiation heating with density 100 W/cm^2. The samples prepared using finely divided, cooled melt and sintered at temperature 1340°C manifest higher mechanical strength and dielectric permittivity than barium titanate samples obtained by ceramic technology.

Key words: piezoelectrics, ferroelectrics, barium titanate, strontium titanate, fusion by a concentrated light flux, synthesis from melt.

It is well known that barium titanate exhibits four crystalline modifications. The high-temperature modification is characterized by perovskite-like cubic structure and is not ferroelectric. The other three are low-temperature modifications, which are distinguished by lower symmetry and are ferroelectric [1, 2]. A characteristic of barium titanate is that it exhibits a stronger piezoelectric effect than quartz [3 – 5]. It is extremely difficult to grow barium titanate crystals of size adequate for cutting plates suitable for applications. At the same time the ferroelectric properties of barium titanate are observed in a wide range of temperatures, which makes it superior to other ferroelectrics. In addition, barium titanate is also a ferroelectric material, i.e., ferroelectric barium titanate with the polycrystalline modification can be obtained by ceramic technology. Material based on strontium titanate $SrTiO_3$ among the virtual ferroelectrics is also of interest.

Spontaneous polarization, which is characteristic of ferroelectrics, is associated with the presence of domains — regions with unidirectional polarization. The domain structure depends on the symmetry of the crystals and is related with the nature and character of the distribution of defects in them. The number and type of defects in the crystal lattice depend on the parameters of synthesis. For this reason every available means to change the process parameters must be used in order to synthesize materials. Investigations of materials synthesis in concentrated radiation fields have shown that concentration of the solar radiation increases the rate of physical-chemical processes of structuring and destruction. Specifically, the possibility of instantaneous action of a concentrated light flux with high density (up to 700 W/cm^2) as well as melting and superfast (to 10^5 K/sec) quenching from melt makes it possible to fix high-temperature phases with different defect density and in a definite nanostate. The defect density in the synthesized material can be controlled by varying the light action parameters. However, comprehensive studies of the interaction of a concentrated light flux with matter have still not revealed the physical-chemical, radiation and thermophysical mechanisms of structuring or destruction occurring in an entire series of materials. It is also of great practical interest not only to obtain but also predict and create new and promising materials.

In the present work we study the synthesis of ferroelectric materials based on barium and strontium titanates in a concentrated high-density light flux.

EXPERIMENTAL MATERIALS AND PROCEDURE

The objects of study were chemically pure grade powdered titanium oxide TiO_2, barium carbonate $BaCO_3$ and strontium carbonate $SrCO_3$ obtained from the Donetsk Chemical Reagents Plant with the appropriate production setup.

The mixtures of the starting materials were prepared in accordance with the stoichiometric composition of barium titanate (mass ratio): $BaCO_3$: TiO = 1.9 : 1 and $SrCO_3$: TiO = 1.8 : 1.

Pellets with diameter 18 mm and thickness 2 mm were prepared from the mixture of the starting materials.

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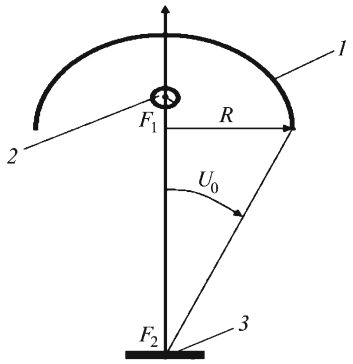

Fig. 1. Diagram of the optical system of the URAN radiation heating setup: *1*) reflector; *2*) xenon lamp; *3*) focal point of optical system.

The pellets were placed in the focal plane of an URAN optical furnace, as shown in Fig. 1.

The radiation source is placed at the near focal point F_1 of the ellipsoid and the receiver at the far focal point F_2. The radiation source is a 10-kW DKSSHRB 10 000 xenon lamp (visible and near-IR ranges of the spectrum with maximum intensity in the range 1.0 – 2.0 μm). The efficiency of such lamps (ratio of the radiation flux to the electric power) is of the order of 60%. An F0A0 13-07 sensor was used to measure the density at the focal point.

The power of the light flux corresponding to the required temperature was determined according to the Stefan–Boltzmann law $Q = (a_s/\varepsilon)\sigma T^4$, where Q is the power of the radiation, a_s and ε are, respectively, the absorption and emission coefficients, σ is the Stefan–Boltzmann constant and T is the temperature.

The phase composition and structural parameters of the samples were determined using a DRON-3 diffractometer with Cu–K_α radiation (λ = 1.5418 Å) and Ni filter. The parameters of the crystal lattices were determined using the Nelson–Rayleigh extrapolation function [6, 7].

The cooled melt was comminuted, after which samples were pressed, sintered in the temperature interval 1000 – 1350°C with soaking time 2 h and allowed to cool freely (A-type samples).

To determine the effect of the light the samples prepared from a stoichiometric mixture of the starting components and sintered in an electric furnace at 1350°C (B-type samples) were used as controls.

It was determined by hygroscopic weighing that the density of the sintered A- and B-type samples was 2.6 and 2.4 g/cm^3, respectively.

RESULTS AND DISCUSSION

The x-ray diffraction pattern of an A-type sample is displayed in Fig. 2. Diffraction reflections of different intensity are clearly seen in it. Analysis showed that such a pattern is described well by the diffraction of x-rays from a tetragonal lattice (RF = 4.6%) with lattice parameters a = 3.99 Å and c = 4.03 Å. The tetragonality factor $\delta = c/a - 1$ was 0.010, attesting to the presence of lattice deformation. The half-widths of the diffraction reflections 002 and 200 were $B_{002} = 24'$ and $B_{200} = 14'$, respectively.

Some differences in the values of the lattice parameters were observed for the B-type samples: a = 3.98 Å and c = 4.01 Å ($\delta = c/a - 1 = 0.007$). It is known that the x-ray diffraction profiles are broadened because of the small size and high defect density of the particles or crystallites. Analysis of the diffraction patterns of strontium showed that such a diffraction pattern corresponds completely to ISTM 5-0634 and represents the cubic modification of the $SrTiO_3$ with lattice parameter a = 3.88 Å.

It is well known that polycrystalline barium titanate is a ceramic with chaotically arranged separate and small single-crystal particles and interlayers of a glassy phase. The amount of the glassy phase as a function of the power of the sintering temperature and, in consequence, the degree of sintering ranges from 1 to several tens of percent by mass. For quite high sintering temperatures (> 1350°C) the mass content of the glassy phase is 1 – 2%. Such a microstructure imparts to the ceramic a high mechanical strength.

Measurements of the deformation under bending of barium titanate samples were performed on an FR-100 apparatus. It was found that samples in the form of 5 × 5 × 10 mm bars start to fail at loads 66 MPa (A-type samples) and 54 MPa (B-type samples), which are very high values.

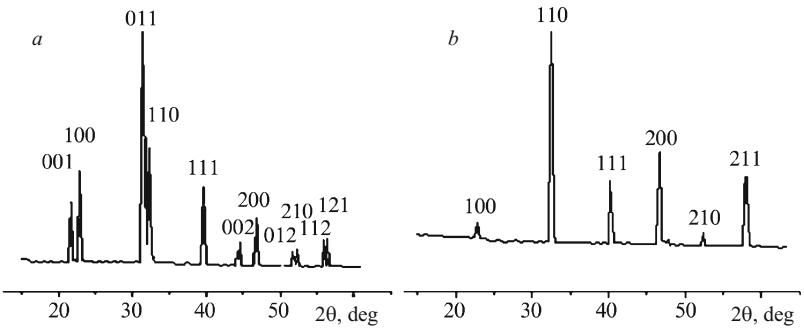

Fig. 2. X-ray diffraction pattern of samples sintered at 1350°C: *a*) $BaTiO_3$ and *b*) $SrTiO_3$.

The barium titanate based ceramic, being a piezoelectric, must possess high dielectric permittivity. The dielectric permittivity was determined by measuring the capacitance of the samples: $\varepsilon = Cd/(\varepsilon_0 S)$, where C is the capacitance of the capacitor and d and S are, respectively, the thickness and surface area of the sample. For barium titanate samples the dielectric permittivity at room temperature was 3800 (A-type samples) and 3400 (B-type samples). The tangent of the angle of dielectric losses is $\tan\delta \approx 0.031$.

CONCLUSIONS

Analysis of the dependence of the structure and properties of barium titanate $BaTiO_3$ and strontium titanate $SrTiO_3$ on the synthesis conditions shows that their structural features and dielectric properties are largely determined by the defect density of the material. Since the light action engenders additional structural defects, which play the main role in the structuring of barium titanate, its crystallization into a perovskite lattice should promote ferroelectric properties.

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